

PROCESS AND SYSTEM FOR PROVIDING ELECTROCHEMICAL PROCESSING SOLUTION
WITH REDUCED OXYGEN AND GAS CONTENT

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RELATED APPLICATIONS:

[0001] This application is a continuation-in-part of US Patent Application serial No. 10/425,782 filed April 29, 2003 (NT-294), which is incorporated herein by reference.

FIELD

[0002] The present invention relates to manufacture of semiconductor integrated circuits and, more particularly to a method for electrochemical deposition or polishing of conductive layers.

BACKGROUND

[0003] Conventional semiconductor devices generally include a semiconductor substrate, such as a silicon substrate, and a plurality of sequentially formed dielectric interlayers such as silicon dioxide and conductive paths or interconnects made of conductive materials. Copper and copper-alloys have recently received considerable attention as interconnect materials because of their superior electro-migration and low resistivity characteristics. Interconnects are usually formed by filling copper in features or cavities etched into the dielectric layers by a metallization process. The preferred method of copper metallization is electroplating. In an integrated circuit, multiple levels of interconnect networks laterally extend with respect to the substrate surface. Interconnects formed in sequential layers can be electrically connected using vias.

[0004] In a typical process, first an insulating layer is formed on the semiconductor substrate. Patterning and etching processes are performed to form features or cavities such as trenches and vias in the insulating layer. Then, a barrier/glue layer and a seed layer are deposited over the patterned surface and a conductor such as copper is electroplated to fill all the features. However, the plating process, in addition to filling the features with copper, also deposits excess copper over the top surface of the substrate. This excess copper is called an "overburden" and needs to be removed during a subsequent process step. In standard plating processes, this overburden copper has a large topography since the Electrochemical Deposition (ECD) process coats large features on the wafer in a conformal manner. Conventionally, after the copper plating, CMP process is employed to first globally planarize this

topographic surface and then to reduce the thickness of the overburden copper layer down to the level of the surface of the barrier layer, which is also later removed leaving conductors only in the cavities.

[0005] During the copper electrodeposition process, specially formulated plating solutions or electrolytes are used. An exemplary electrolyte contains water, acid (such as sulfuric acid), ionic species of copper, chloride ions and certain additives, which affect the properties and the plating behavior of the deposited material. Typical electroplating baths contain at least two of the three types of commercially available additives such as accelerators, suppressors and levelers.

[0006] Electroplating solutions such as the commonly used copper sulfate solutions employed for copper film deposition naturally contain dissolved air since they are in contact with air. While in use in plating tools these electrolytes may further get saturated with air since they are often cycled between the plating cell and an electrolyte tank. After being used in the plating cell for plating copper onto the workpiece surface, electrolyte is directed to the main tank, and after filtration and chemical composition adjustment, it is pumped into the plating cell. Such re-cycling minimizes electrolyte waste, however, at the same time it increases air dissolution into the electrolyte. In some prior art approaches, a nitrogen blanket has been used over the electrolyte tank and other parts of the system to minimize exposure of electrolyte surface to air and specifically to the oxygen in the air. There have also been methods that involved injecting or bubbling nitrogen gas into the electrolyte to specifically reduce the dissolved oxygen content of the electrolyte. Such efforts can reduce the concentration of dissolved oxygen in the solution, however it does not reduce the total dissolved gas content of the solution. In fact, such approaches can enhance the dissolution of the used gas, such as nitrogen, into the electrolyte. In other words, gas content in the electrolyte would still be high, although its chemical composition would be different.

[0007] Dissolved gas in plating electrolytes creates several problems. First, dissolved gas in any liquid causes initiation and growth of bubbles on surfaces touching the liquid. For example, when a workpiece, such as a semiconductor wafer is immersed into a copper-plating electrolyte with dissolved gas in it, micro-bubbles of gas often spontaneously initiate on the surface of the wafer. Initiation and growth rate of such micro-bubbles are expected to be a function of the degree of saturation of the liquid by the gas. Highly agitated electrolytes in the presence of a gas, such as air, are highly saturated with air and therefore bubbles form on surfaces touching such electrolytes very easily.

[0008] Degassing of the plating electrolyte used in electrochemical plating or electrochemical etching/polishing processes reduces the dissolved air content of the electrolyte. Since air contains oxygen, dissolved oxygen content is also reduced in the process.

[0009] Reducing, even further, the oxygen content of electrolytes used in electrochemical processes such as electroplating is desirable. Reduced oxygen content in the electrolyte reduces oxidation of the organic additives (such as brighteners or accelerators, suppressors, levelers etc), which are commonly included in the formulation of such solutions. Reduction of oxidation of additives, in turn, extends the lifetime of organic additives and reduces overall process cost. Organic additives, once oxidized, lose their ability to provide good properties to the deposited layer and thus need to be replenished. During electrochemical deposition processes, as thin seed layers enter an electrolyte, the seed layers are chemically attacked by the electrolyte if the electrolyte contains high level of dissolved oxygen. Electrolytes containing dissolved oxygen have stronger oxidizing property. Therefore, their chemical etching strength is high. Further, if the process solution is a deposition solution, such as a copper electrochemical deposition solution or a copper electroless deposition solution, films grown using electrolytes with less dissolved oxygen are expected to contain less oxygen. Reduction of oxygen impurity in the deposited layer, such as a copper layer, on the other hand, increases its grain size, especially after the layer is annealed. Less oxide in the copper layer and larger grain size, reduce its electrical resistivity, which is very important in electronics applications, such as interconnect applications.

[0010] Review of aforementioned factors, therefore, indicates that there is a need to reduce the oxygen content of electrochemical processing solutions and at the same time reduce their gas content.

SUMMARY

[0011] Present invention provides a method and a system for removing oxygen and other gasses, or at least minimizing their content, from the process solutions used in wet chemical or electrochemical processes. The present invention substantially removes dissolved oxygen from the process solution by deoxygenating the process solution in a deoxygenator and then degassing it in a degasser to further remove, if any, remaining oxygen along with other dissolved gasses in the process solution. The deoxygenator removes oxygen by bubbling a treatment gas into the process solution. In the following degassing step, the treatment gas is also removed from the process solution along with other gasses and the remaining oxygen. After deoxygenating and degassing, the process solution is used for wet processing, such as electrodepositing copper onto, a conductive surface of a semiconductor wafer.

[0012] In an aspect of the present invention provides a method of electrochemically processing a conductive surface of a workpiece using a process solution. The method first includes deoxygenating

the process solution to substantially remove oxygen from the process solution. After deoxygenating, the process solution is degassed to remove gasses. Next, the surface of the workpiece is electrochemically processed with the process solution that is deoxygenated and degassed.

[0013] In another aspect of the present invention, a system for removing gasses from a process solution, that is used to process a workpiece surface, is provided. The system includes a holding tank for holding the process solution, a deoxygenator for receiving the process solution from the holding tank to substantially reduce oxygen content in the process solution, and a degasser for receiving the process solution, which is deoxygenated, from the deoxygenator to remove substantially all gases from the process solution.

[0014] These and other features and advantages of the present invention will be described below with reference to the associated drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] Figure 1 is a schematic illustration of an electrochemical mechanical processing system;

[0016] Figure 2 is a schematic illustration of an embodiment of a system of the present invention including a deoxygenator and a degasser; and

[0017] Figure 3 is a schematic illustration of another embodiment of a system of the present invention including a deoxygenator and a degasser.

DETAILED DESCRIPTION

[0018] Present invention provides a method and a system for substantially removing dissolved gas and oxygen content from process solutions used in wet processes. Wet processes may include electrochemical processes (such as electrochemical deposition), electrochemical mechanical processes (such as electrochemical mechanical deposition or polishing), electroless processes (such as electroless deposition), chemical processes (such as chemical etching) and chemical mechanical processes (such as chemical mechanical polishing). The present invention substantially reduces the oxygen content of the process solution by deoxygenating the process solution in a deoxygenator and then degassing it in a degasser to further reduce the oxygen content along with other dissolved gasses in the process solution.

[0019] A process of the present invention may be exemplified by deoxygenating and degassing a process solution used in an electrochemical mechanical processing (ECMPR) system or station 50 shown in Figure 1.

[0020] The (ECMPR) system 50 includes a carrier head 53, a pad 54 having openings 56, and a carrier head 53. The carrier head holds a wafer 52 with a front surface 51 to process in system 50. The carrier head 53 can rotate and move the wafer vertically (z-direction) and laterally (x or y directions). The pad 54 is supported by a perforated support structure 58 having openings 59. A filter 60 is placed under the support structure or between the support structure and the pad. As shown in Figure 1, the width and length of the pad 54 may be such designed that the width of the pad may be shorter than the diameter of the wafer. The length of the pad 54 may be longer than the diameter of the wafer 52. Electrical contacts 62 may touch the edge of the wafer 52 and connect the surface 51 to a terminal of a power supply 63. A process solution 64, which is contained in a chamber 66, is delivered to the space between the filter 60 and an electrode 68. The electrode 68 is connected to a terminal of the power supply. During a deposition process, the electrode 68 is an anode that is connected to the positive terminal of the power supply while the surface 51 of the wafer 52 is negatively polarized by the other terminal of the power supply. During material removal processes such as electrochemical mechanical polishing, however, the electrode 68 is polarized negatively while the wafer surface is polarized positively. The solution passes through the filter, the openings in the support structure as well as the pad, and wets the surface of the wafer. The process solution is delivered to the chamber 66 through a solution inlet 64 from a process solution tank (see Figures 2 and 3). The used process solution 70 leaves the chamber from an upper edge of the chamber 66 and circulated back to the process solution tank. The process solution may be an electroplating solution for electrochemical deposition or electrochemical mechanical deposition processes, and an electropolishing or electroetching solution for the electrochemical polishing or electrochemical mechanical polishing processes. Exemplary deoxygenating and degassing procedures for the process solution will be described with help of Figures 2 and 3. It should be noted that although an ECMPR system and process is selected to describe the invention, the invention could be used in any electroplating, electroless plating, chemical etching or electropolishing process as mentioned above.

[0021] As shown in Figure 2, a processing system 100 may comprise a holding tank or a solution tank 102 that is connected to a wet processing unit comprising a number of wet processing stations 104. The wet processing stations in Figures 2 and 3 may be electrochemical process stations, electrochemical mechanical process stations, chemical process stations, chemical mechanical process stations, or any combination thereof. Solution tank 102 is also connected to a pump 105, a deoxygenator 106 and a degasser 108. In this embodiment, a process solution 110 in the solution tank undergoes two cycling operations. The process solution is filled into the tank through an inlet 103. In

a first cycling operation, the pump 105 delivers the solution 110 in the tank to the deoxygenator 106 and the degasser through a first line 112 with a first solution flow 111A. In this respect, the process solution 110 is first deoxygenated in the deoxygenator to reduce the dissolved oxygen content in it. Deoxygenated process solution is then degassed in the degasser 108 and delivered to a second line 114 with a second solution flow 111B. Deoxygenator may increase the overall gas content in the solution as it reduces the content of oxygen. For example, some deoxygenators introduce inert gases such as nitrogen (N₂), argon (Ar), helium (He), or even hydrogen (H₂) into the solution. Treatment gases may be introduced by sparging, bubbling or injecting a gas into the process solution. Such a treatment knocks out or sweeps the oxygen in the solution, but during the process, the treatment gas itself may dissolve into the solution. Therefore, after the deoxygenation process, the overall dissolved oxygen content in the solution is reduced but the total dissolved gas content is the same or even higher due to the introduced gas. To get rid of the excessive gas in the solution, the solution is directed next into the degasser 108. Degasser takes out the excess gas along with an additional portion of the remaining oxygen. Excess gas may comprise any undesirable dissolved or undissolved gas in the solution. In this case, Excess gases comprise treatment gas and other dissolved gases that have been already in the process solution. This way a solution with both low gas and low oxygen content is obtained, that could not be obtained by the degasser only or the deoxygenator only. As an example, if we reference 100% gas and 100% oxygen content for an electrolyte that is not treated, after the deoxygenation, dissolved oxygen content may go down to 20% and dissolved gas content may still be 100%. After the degassing step, the dissolved gas content may go down to 15% and the oxygen content may be reduced to less than 5%. The second line 114 delivers the process solution in second solution flow 111B, which is deoxygenated and degassed, back to the solution tank 102. This cycle is either continuous or intermittent. In other words, deoxygenating and degassing may be carried out either continuously or only part of the time.

[0022] In a second cycling operation, through a third line 116, the process solution 110 with very low oxygen and gas content is delivered to the wet processing stations 104 with a third solution flow 111C. Delivery of the process solution may be provided with a pump (not shown) in the third line. The delivery may be performed through an intake manifold 118 connecting the line 116 to each process station 104. The intake manifold 118 may include valves (not shown) to switch on and off the third solution flow 111C to each station. Used process solution from each station is received by a solution exit manifold 120 and is delivered to a fourth line 122 as a fourth solution flow 111D. The fourth line 122 delivers the fourth solution flow 111D, which is the used process solution, back to the

process solution tank where additives may be added to replenish the process solution. Alternatively, the replenishment may be done in a replenishment tank (not shown). In this case, the fourth solution flow may be first delivered into a replenishment tank. Due to the process that is performed using the process solution in the stations, the oxygen content and the gas content of the process solution in the fourth flow may be high. After filtering the solution and adding additives in the replenishment tank, the process solution is delivered to the solution tank to mix with the existing solution in the solution tank. The delivery of the fourth flow or the used solution into the solution tank may be done intermittently or continuously to keep the oxygen and gas levels in the process solution under predetermined limits.

[0023] The process of the present invention keeps the oxygen and other gas content in the process solution low. During the process, both cycling operations run simultaneous or in discontinuous modes. In simultaneous mode, cycling speed of the first cycling operation is kept substantially higher than the second cycling operation to preserve the levels of oxygen and gas in predetermined limits in the solution tank. In discontinuous mode, the fourth line 122 may be turned off periodically by a valve (not shown) to allow first cycling operation to deoxygenate and degas the process solution in the tank 102 and to deliver this solution to the third line 116 for processing. As the fourth line 122 is turned off the used solution, as the fourth flow 111D, in this line may be flowed into a temporary storage tank (not shown) so that when the fourth line is open again the solution in the temporary solution tank can be delivered back to the fourth line or into the solution tank. As the fourth line is opened, the third line 116 is turned off so that the used solution can be delivered to the solution tank to be deoxygenated and degassed by the first cycling operation. In this case, since the used solution is mixed with the solution having very low oxygen and gas levels, the oxygenating and degassing take less time. Once the deoxygenating and degassing are complete, the third line is opened and the fourth line is turned off as described above for another process run. Of course, it is possible to use the invention in a mode where the degassed and deoxygenated process solution is used at the process stations 104 and then discarded instead of returning the used solution to the solution tank 102.

[0024] As shown in Figure 3, another processing system 200 according to an embodiment of the present invention uses degassed process solution. The system 200 may comprise a solution tank 202 that is connected to a wet processing unit comprising a number of wet processing stations 204. In this embodiment, a deoxygenator 206 and a degasser 208 are connected between the solution tank 202 and the processing stations 204. In operation, a process solution 210 in the tank is first delivered to the deoxygenator and then the degasser through a first line 212 as a first solution flow 211A. The process

solution is filled into the tank through an inlet 203. The process solution is deoxygenated and delivered to a second line 214 as a second solution flow 211B. The second line 214 delivers the second solution flow 211B of process solution, which is deoxygenated and degassed, to the processing stations 204. The delivery may be performed through an intake manifold 216 connecting the line 214 to each processing station 204. The intake manifold 216 may include valves (not shown) to switch on and off the second solution flow 211B to each station. Used process solution from each station is received by a solution exit manifold 218 as a third solution flow 211C and is delivered to a third line 220 for recycling. The third line 220 delivers the third flow 211C, which is the used solution, back to the solution tank to be replenished and degassed. Alternatively, the replenishment may be done in a replenishment tank (not shown). In this case, the third solution flow may be first delivered into a replenishment tank and then to the solution tank. After filtering the solution and adding additives in the replenishment tank, the process solution is delivered to the solution tank. It should be noted that, in system 200, instead of one degasser 208, multiple degassers may be used by connecting each to the lines of the manifold that are connected to the processing stations 204.

[0025] It should be noted that Figures 2 and 3 show the system only in a high level form without necessarily showing all the valves, pumps, and filtration arrangements that may be employed. Further, in such systems, instead of one deoxygenator and one degasser, multiple deoxygenators and degassers may be used. In one embodiment, both or one of the deoxygenator and degasser may be placed in the solution tank itself. Further, the deoxygenator and degasser may be separately connected to the holding tank. In this approach, for example, in a first circulation, the deoxygenator may receive the process solution from a first intake line, and after deoxygenating the solution, the deoxygenated solution may be returned to the holding tank through a second return line. Similarly, in a second circulation, the process solution is received from a second intake line and degassed. After degassing, the solution is returned to the holding tank through a second return line. Placement of deoxygenator and degassers in Figures 2 and 3 may also be varied.

[0026] Although various preferred embodiments and the best mode have been described in detail above, those skilled in the art will readily appreciate that many modifications of the exemplary embodiment are possible without materially departing from the novel teachings and advantages of this invention.